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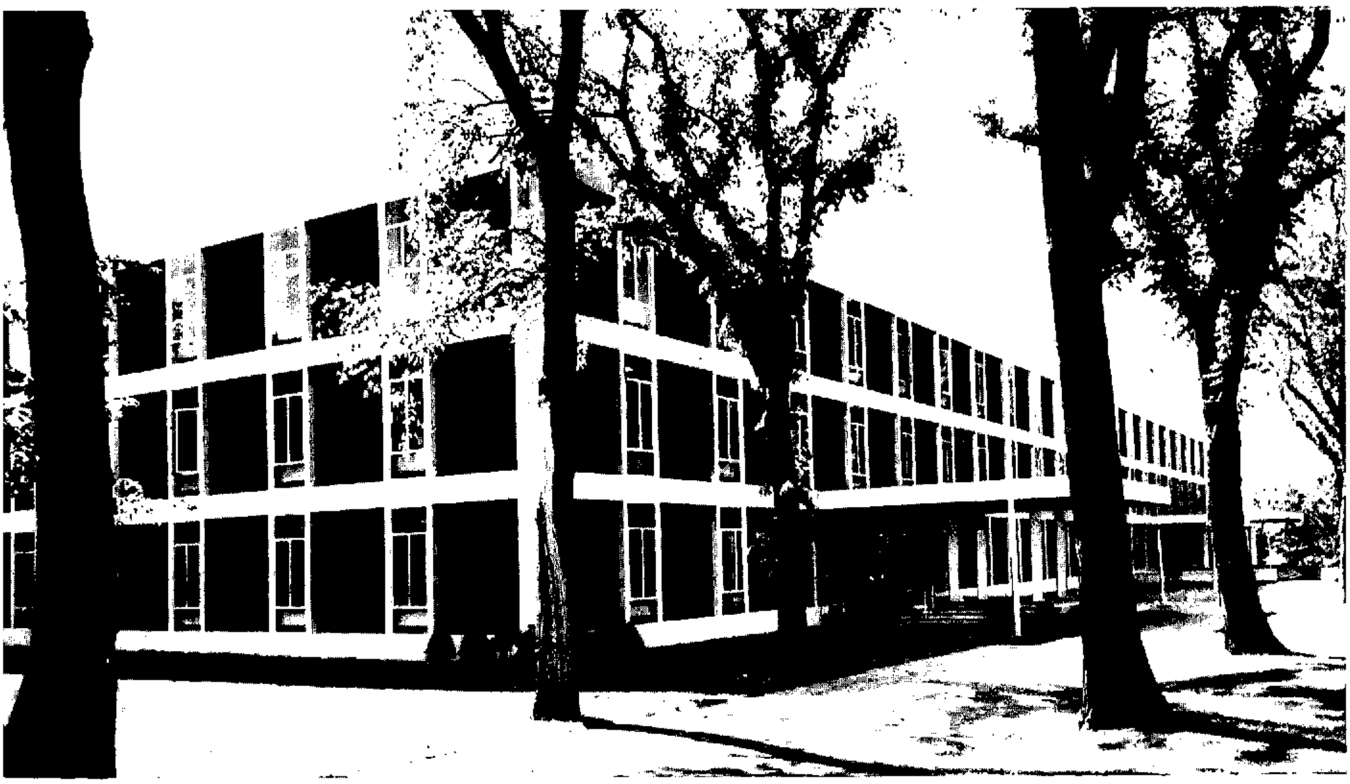

SEMI-ANNUAL PROGRESS REPORT

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Grant No.

NGL 33-018-003

Rensselaer Polytechnic Institute

Troy, New York

I

November 1973

TABLE OF CONTENTS

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Semi-Annual Progress Report
National Aeronautics and Space Administration Grant NGL 33-018-003
March 1, 1973 - August 31, 1973

INTRODUCTION

This twenty-fifth Semi-Annual Report presents up-to-date information on research projects currently being pursued with National Aeronautics and Space Administration support under Grant No. NGL 33-018-003. Its contents are organized in a slightly different way than in the last report. There are now three sections rather than four. The contents of the section, "Processing and Fabrication," have been absorbed by two of the remaining three sections; these two have also been wholly or partially renamed. The three sections now are "Materials for Aerospace Applications - Electrical," "Materials for Aerospace Applications - Structural and High Temperature," and "Physical Properties and Structure of Aerospace Materials." This reorganization is felt to represent better the material presented.

The individual research studies reported herein are the results of those projected in Rensselaer's proposal dated October 1972. Each section is preceded by a semi-technical introduction.

1-A

MATERIALS FOR AEROSPACE APPLICATIONS - ELECTRICAL

MATERIALS FOR AEROSPACE APPLICATIONS - ELECTRICAL

The projects in this section are concerned primarily with the electrical properties of glasses, oxides and metals. In general, the emphasis is on the physical understanding of the observed phenomena in terms of simple models.

New insight into the behavior and environment of the iron atoms included in $BaO-B_2O_3$ glasses is being obtained by use of the Mössbauer technique as a microscopic probe. Under heat treatment, one can follow the precipitation of ferric oxide and the change in local environment of the iron still in solution. Low temperature magnetic susceptibility measurements are being prepared.

The studies of polaron hopping in NiO is continuing by the use of transport measurements at the Nèel temperature and of optical excitation to explore the photoconductive response, also as a function of temperature.

The calculations of ad-atom binding to the surface of a free-electron metal are giving preliminary results in rough agreement with predictions based on free surface energy considerations.

MÖSSBAUER EFFECT STUDIES OF THE MICROSCOPIC NATURE OF SEMI-CONDUCTING OXIDE GLASSES CONTAINING TRANSITION METAL IONS

Senior Investigator: M. P. Maley

The glass system $BaO-B_2O_3$ containing dissolved Fe_2O_3 has been extensively studied at R.P.I. by R. K. MacCrone. Electrical resistivity, electron spin resonance, and magnetic susceptibility measurements have indicated a correlation between the electrical and magnetic properties of these glasses. In particular, the magnetic behavior is extremely sensitive to the microstructure of the glass, clustering or pairing of iron atoms and the valence ratio of Fe^{2+}/Fe^{3+}. These same factors strongly influence the ac and dc conductivity. The Mössbauer effect allows an examination of the microscopic environment of the iron to be made which does not average over several different kinds of sites.

Presently, studies have been made of these glasses containing Fe concentrations ranging from 0.5 mole % to 10.0 mole %. In general, at room temperature the Mössbauer spectra exhibit a predominant well resolved quadrupole doublet with quadrupole splitting $\sim$ 1.1 mm/sec and with isomer shifts (relative to Fe-metal) ranging from 0.31 - 0.35 mm/sec. These values are consistent with those expected for Fe^{3+} in a highly distorted tetrahedrally coordinated site, but are much larger than isomer shifts found for silicate glasses. The intermediate values for these isomer shifts suggests the possibility that a combination of tetrahedral (with smaller isomer shifts) and octahedral sites is present.

Upon heat treatment, the more concentrated glasses exhibit well resolved 6-line patterns which coincide in line position with the magnetic hyperfine pattern of α-Fe_2O_3. In addition, a quadrupole doublet due to the still dissolved Fe is also present. This doublet has a reduced quadrupole splitting of 0.69 mm/sec and a larger isomer shift of .39 mm/sec, which coincides with that of the octahedral sites in Fe_2O_3. Thus, it appears that while the heat treatment has induced precipitation of crystalline

Fe_2O_3, the remaining dissolved iron is in a more symmetric site consistent with octahedral coordination. These effects are being studied as a function of heat treatment and iron concentration with the intent of understanding the separation process.

Low temperature measurements down to 4 K show no evidence of magnetic ordering or slow relaxation effects for Fe concentrations where 3% $<C<$ 8%, in the quenched glasses. (C is the mole % of iron) At 10%, magnetic ordering and/or superparamagnetic effects are apparent at 4 K, while 2% Fe glasses show relaxation broadening. A temperature control system now under construction will allow magnetic susceptibility measurements to be made by measuring Mössbauer effect hyperfine splittings in applied magnetic fields. This will allow the determination of the magnetic moments of the individual Fe ions and clusters present in these glasses.

ELECTRON HOPPING AND IONIC DEFECTS IN TRANSITION METAL COMPOUNDS

Senior Investigator: R. K. MacCrone

Bound Polarons in TiO_2

Work continues on the analysis of the temperature dependence of the polaron bandwidth, found to be of the form $J = J_o \exp(\Delta/T)$ in qualitative agreement with polaron theory.

We are presently extending measurements to higher magnetic field values.

Conduction in NiO

We have recently obtained very precise thermo-electric data, as well as dc and ac conductivity measurements. These results indicate strong discontinuities at the Nèel temperature, which suggests that d-state conductive processes are significant in these carefully compensated specimens. By numerical analysis, we hope to demonstrate the existence of d-state hopping in these specimens and determine the polaron parameters.

Work is progressing on the effects of optical excitation on the electrical properties. To date, we have discovered that dipolar (bound polaron) sites are $\sim$ .6 eV from some other states and that photoconduction may be induced whose temperature dependence will again determine the mode of conduction.

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Work has begun on Fe_2O_3, investigating the effect of the Morin transition of the spin direction on the transport behavior.

ELECTROMIGRATION AND SURFACE MOBILITY

Senior Investigator: H. B. Huntington

The computation of the forces holding an ad-atom to the (close-packed) surface of a simple metal are proceeding. The technique is to vary the charge density distribution of the ad-atom valence electron(s) and of the metallic electrons to minimize the energy in the density approximation. The present effort is concentrated on distortions of the valence electron distribution by displacement and deformations intended to "flatten" the valence electron to the surface. For atom and surface fitted to the case of sodium, simply bringing the atom to the surface results in a binding energy of about 1/3 ev. This binding energy is comparable to the twice surface energy per atom (0.15 ev) as determined experimentally. The equilibrium position falls at a distance from the geometrical surface about 15% greater than one half the distance between close-packed planes. This distance may decrease and binding energy increase with improved minimization.

We plan to carry through similar calculations for the electron densities of several metals and eventually to structure the jellium metals of higher density for at least the first atom layer.

6-A

MATERIALS FOR AEROSPACE APPLICATIONS - STRUCTURAL AND HIGH TEMPERATURE

MATERIALS FOR AEROSPACE APPLICATIONS - STRUCTURAL AND HIGH TEMPERATURE

The concern of the research programs reported on in this section has been the determination of structure property relationships in a broad sampling of crystalline and amorphous systems which have applications primarily as structural materials. Analyses relating processing variables, microstructures, and composition to the engineering properties of these materials are described. A brief summary of the overall research effort in this area is given below and more detailed individual reports are presented following this introduction.

Vapor deposited silicon carbide has recognized potential for high temperature oxidative environment applications. However, the presences of residual stresses inherent to vapor depositiontechniques can cause a decrease of the ultimate strength of silicon carbide. A detail characterization of the residual stresses as a function of deposition parameters was therefore obtained. These data provide the necessary information to allow for new or alternate processing techniques.

The study of the effects of second phase particles on the mechanical behavior of crystalline solids has focussed upon defining the localized stress state and determining the effect of interface strength on the mechanical properties of dispersion strengthened alloys such as TD-nickel and TD-nichrome. Thermal shock followed by creep studies, direct observation in transmission electron microscopy of the elastic stresses around the particles and computer programs to analyze dislocation particle interactions are experimental methods that have been employed.

Mechanical aging studies of several different polymers prepared by both slow cooling and by quenching from above the glass transition temperature showed that the effect of strain was found to accelerate the approach of the quenched samples to the slow cooled sample behavior. The rate of aging was found to correlate with the glass transition temperature.

A nickel-base superalloy, Udimet 700, which due to hot cracking and strain age cracking phenomena is difficult to fusion weld, is being studied as a potential candidate for application of diffusion bonding techniques. In order that suitable procedures and parameters be developed, the kinetics of the precipitation and of diffusion bonding are being studied, employing controlled time, temperature, and mechanical restraint conditions. The high temperature tensile and creep ductility of Ni-base super alloys as a function of the carbide morphology in the alloy is a new program of investigation that has recently been started.

The study of high cycle fatigue in lamellar $Al-Al_3Ni$ as compared to fibrous $Al-Al_3Ni$ eutectics has shown that specimens grown under different rates have similar fatigue lives and exhibit common features in terms of the fractography of the fatigue failure.

The analysis of composition microsegregation as a function of heat treatment in three different titanium alloys (Ti-8Al-1V-1Mo, Ti-6Al-4V, Ti-13Cr-11V-3Al) has shown that microsegregation of the alloying elements occurs within the microstructure. The distribution of aluminum and vanadium was determined and correlated with the specimens' microstructure.

The temperature-composition phase diagram for GeSe-GeTe systems has been under study for room temperature and will be continued at higher temperatures. This information is a prerequisite for the knowledge required to grow mixed single crystals in this system by the vapor transport technique.

CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE

Senior Investigator: R. J. Diefendorf

A problem inherent to vapor deposited materials, in general, is that of residual stress. The present project period was utilized to study the relationship of deposition conditions to residual stress in chemically vapor deposited silicon carbide. Whether this material is to be used as a coating or as a structural part, strains, due to the growth process itself, arise during deposition and decrease the ultimate strength of the material.

Silicon carbide was deposited along the bores of one inch graphite deposition tube from methyltrichlorosilane-hydrogen mixtures over a wide range of deposition conditions. After deposition, the graphite substrate was removed and the remaining silicon carbide hollow cylinders were sectioned into one-inch diameter rings, one inch long. These rings, sectioned axially, changed diameter due to the sign of the residual stress. The residual stress was calculated and related back to the deposition conditions.

In all cases, the sectioned rings decreased in diameter once they were split, indicating that within the wide range of deposition conditions that produced pure silicon carbide, the last deposited surface, or internal surface, was in tension. The residual stress was related to deposition temperature, pressure, reactant concentration, deposit thickness, flow rate or velocity of the deposition gases, and deposition rate by statistical analysis techniques. Both the temperature of deposition and the deposition rate appeared to exhibit the greatest correlation with residual stress. At a particular temperature, a linear dependence on deposition rate occurred for the residual stress. This was further evidenced by an examination of the residual stress along the complete length of the deposit as removed from the deposition tube. At sections of the tube where the deposit was thickest, the residual stress was maximum, decreasing with the deposition rate toward other parts of the tube.

This dependence of residual stress on deposition rate arises from the time allowed an individual atom to migrate around upon the surface of the deposit during deposition. At low deposition rates, an individual atom has time to attach itself to a growing front of an individual crystallite, therefore forming a more ordered, crystalline deposit. At higher deposition rates, new layers are being added so fast that a more disordered structure is "frozen in" giving rise to stresses.

The consequences of this can be handled in either of two ways. If constrained shapes are to be made, low deposition rates are mandatory to minimize residual stresses. A more logical approach would be to make use of the sign of the residual stress to minimize applied stresses on the desired part.

DISPERSION STRENGTHENING MECHANISMS

Senior Investigator: G. S. Ansell

This research program has been concerned with the effects of second-phase particles on the mechanical behavior of crystalline solids. During this program period, studies were continued to detail the effect of the localized stress state around second-phase particles upon the mechanical properties of two phase alloys. This study has been proceeding along several related paths.

One aspect of the program has been to study the effects of combined thermal stresses with superimposed loading on the mechanical behavior of TD-Nickel and TD-Nichrome. Here, thermal shock applied to an alloy system where the metal matrix expands away from the thoria particle is used to induce particle-matrix interface failure. This method is being utilized primarily to study the effect of interface failure on the stress-rupture and creep behavior of these alloys. The results to date indicate that thermal shock prior to testing increases the strain rate sensitivity to stress while reducing the stress rupture life. The temperature dependence of the creep rate appears unaffected by prior thermal shock.

The second approach taken in this study has been to determine directly the interface strength between dispersed-phase particles and metal matrices. The method used here is to strain thin-foil specimens of two-phase alloys within the electron microscope. By following the development of the elastic stresses around the second-phase particles, using strain contrast as an indicator, the point of interface failure (loss of contrast) can be directly related to the stress state producing failure. Preliminary studies, using this device, are being conducted on the nickel-thoria system and other alloy systems.

The third area studied in this program has been to characterize quantitatively the localized stress state in the matrix surrounding second-phase particles in a tensile-loaded alloy as a function of particle-matrix modulus ratio, lattice or coherency strains, and particle-matrix volumetric misfit. The purpose of this analysis is to extend our investigation of the localized stress condition from interface behavior to determination of dislocation-particle interactions during plastic deformation. A computer program has been set up to analyze the effects of these interactive stress fields upon two specific types of dislocation-particle interactions, dislocation bowing and cross-slip. While these studies are still in progress, the results to date indicate that particle cross-slip is not a usual bypass mode during the deformation of two-phase alloys, while particle bypass by bowing occurs at a higher stress than would be predicted by the usual evaluation of the Orowan mechanism.

MECHANICAL PROPERTIES OF POLYMERS

Senior Investigator: S. S. Sternstein

Mechanical aging studies have been performed on polymethyl methacrylate (PMMA), plasticized and unplasticized polyvinyl chloride (PVC), and polycarbonate (PC). Samples were prepared by both slow cooling and quenching from well above the glass transition temperature. After various delay times at room temperature, each sample was subjected to a series of stress relaxation tests which consisted of repetitive cycles of constant strain followed by stress free recovery for twice the time under strain.

In all cases it was found that the effect of strain was to accelerate the approach of the quenched samples to the slow cooled sample behavior. Isochronous comparisons of stress relaxation rates showed that application of 0.5% strain for 500 minutes produces more aging than 10,000 minutes at no strain. The rate of aging was found to correlate with the glass transition temperature of each sample in that master relaxation curves could be obtained by superposition with respect to reduced time, with the reduction factor dependent on the mechanical history and temperature (below the glass transition). These results suggest that aging of glassy polymers can be treated by reduced state variables in much the same way as above the glass transition, but with due account of the mechanical and thermal history.

Further studies will attempt to relate these results to yield and impact behavior of the glassy polymers.

DIFFUSION BONDING OF UDIMET 700

Senior Investigator: W. F. Savage

Nickel-base superalloys containing combined titanium plus aluminum contents greater than approximately 6% are generally considered difficult to weld. Therefore it is not surprising that Udimet 700, with 3.5% Ti and 4% Al is notoriously difficult to weld. The problems encountered with fusion welding of this alloy include:

a. Hot-cracking during welding
b. Strain-age cracking, a form of cracking which occurs during post-weld heat treatment in many precipitation-hardenable nickel-base alloys.

One method of controlling these problems would appear to be the application of a technique for bonding in the solid state known as diffusion bonding.

In order to develop suitable procedures for diffusion bonding Udimet 700, work has been initiated in two areas as follows:

1. The kinetics of the precipitation and solutionizing reactions are being explored with the R.P.I. Gleeble. The experiments are designed to show the effects of both time and temperature on those reactions under various degrees of externally imposed mechanical restraint. This information is vital to a better understanding of the origin and nature of strain-age cracking.
2. The kinetics of diffusion bonding is also being explored with the aid of the R.P.I. Gleeble. A fixture has been constructed for holding 0.250-in. dia. specimens in axial alignment and applying a readily controlled axial load. The fixture is connected to the R.P.I. Gleeble and the time-temperature cycle experienced at the weld interface can be programmed at will. In this fashion,

the effects of time, temperature and the compressive stress at the weld interface on the diffusion bonding process are being studied.

The results to date, although only preliminary, show considerable promise. Therefore, during the next six-month period these parallel investigations will be continued.

CARBIDES AND HIGH TEMPERATURE DUCTILITY OF NICKEL-BASE SUPERALLOYS

Senior Investigator: G. S. Ansell
(Material prepared by N. S. Stoloff, a participating investigator)

This research program was started in an attempt to determine the precise effects of carbide morphology on elevated-temperature tensile and creep-rupture ductility of Ni-base superalloys. It is hoped that the proper carbide morphology will eliminate some of the ductility loss manifested as a ductility minimum in the region of 1500°F. Inconel X-750 and Inconel 600 are the two commercial alloys chosen for the study. The major difference between these alloys is that Inconel X-750 is hardened by γ' Ni_3Al while Inconel 600 does not have this strengthening phase.

The necessary heat treatments to obtain no carbides, globular carbides, or cellular carbides at the grain boundaries have all been determined and the results checked by the use of optical microscopy. Transmission electron microscopy was initially used to observe the carbides; however, replicas were found to be much more effective. Negative replicas produced from acetyl cellulose and coated with Cr-C were used for examination of carbide morphology and γ' - carbide relationships.

Preliminary tests have been conducted on the "Gleeble," (a device capable of rapid heating rates) as a specimen design test and a systems check for the argon atmosphere chamber and the gripping mechanism. Metallographic examination of some fractured samples showed both wedge and spherical shaped voids.

The next phase of the program is to determine the precise temperature of the ductility minimum for both alloys and then test at these respective temperatures with different carbide distributions. Finally, specimens strained to a point prior to fracture will be examined to determine regions of crack initiation.

DEFORMATION AND FRACTURE OF CONTROLLED EUTECTICS

Senior Investigator: G. S. Ansell
(Material prepared by N. S. Stoloff, a participating investigator)

High cycle fatigue tests, on lamellar Al-Al_3Ni specimens grown at 0.5 cm/hr, have shown similar fatigue lives to fibrous Al-Al_3Ni grown at 3.5 cm/hr and 11 cm/hr. Electron scanning fractography of the fatigue failures has demonstrated that specimens grown at different speeds exhibit common features. In all cases, the fatigue-cracked areas were very jagged, due to crack propogation parallel to the reinforcing whiskers; tensile overload areas were relatively smooth, dimpled areas caused by brittle whiskers failure and ductile failure of the matrix.

Metallographic cross sections of the fatigue-cracked areas demonstrated the ability of the reinforcing phase to redirect the fatigue crack on long winding paths around the discontinuous fibers. Throughout the fatigue area, smaller areas of tensile failures acted as transitions between steep crack paths.

Two-stage replicas made of specimen surfaces during early stages of their fatigue lives have exhibited intense slip bands on the matrix surface, and random brittle fiber failures. Whether the fiber breaks or intense slip offsets can be linked to crack nucleation has yet to be determined. It is observed, however, that cracks are present within the first 10% of the specimen life.

Additional replica work will be done to identify crack nucleation sites. High temperature fatigue tests will commence on a recently completed apparatus, and an electron transmission study will be continued on successfully prepared foils, in the expectation that dislocation substructures, as related to interfiber spacing and interphase boundaries, will be identified.

An investigation of the Al-$CuAl_2$ directionally solidified eutectic has been continuing. Preliminary work on the fatigue behavior of the eutectic in the as-grown and in the solution-and-aged conditions has been completed. Documentation of microstructure, as a function of growth rate, was also done. From this work, an S-N curve with reasonable scatter and a plot of lamellar spacing versus growth rate were produced.

ANALYSIS OF THE MICROSTRUCTURE AND THE COMPOSITIONAL MICROSEGREGATION AT GRAIN BOUNDARIES OF STRUCTURAL ALLOYS SUSCEPTIBLE TO LOCALIZED CORROSION ATTACK

Senior Investigator: Gary Judd

The three commercial titanium alloys Ti-8Al-1V-1Mo, Ti-6Al-4V and Ti-13Cr-11V-3Al were subjected to the following common heat treatments:

Alloy	Heat Treatment	Designation
Ti-8Al-1V-1Mo	790°C, 1 hr., Air cool	811-1
Ti-8Al-1V-1Mo	790°C, 1 hr., Furnace cool	811-16
Ti-8Al-1V-1Mo	900°C, 1 hr., Air cool	811-15
Ti-8Al-1V-1Mo	900°C, 1 hr., Furnace cool	811-5
Ti-6Al-4V	840°C, 2 hr., Furnace cool to 700°C, 2 hr., Air cool	64-3
Ti-6Al-4V	840°C, 2 hr., Furnace cool to 700°C, 2 hr., Furnace cool	64-18
Ti-13Cr-11V-3Al	790°C, 1/4 hr., Water quench and 480°C, 22 hr., Air cool	13-11-3-7

Specimens of these three commercial titanium alloys were then subjected to an alpha phase stain etch consisting of a solution of 0.5ml hydrofluoric acid in 100ml distilled water. Each specimen was swabbed for nearly ten seconds to highlight the alpha phase areas. Back-scattered electron imaging on an electron probe microanalyzer, EPM, was employed to identify the microstructures of each specimen. The microprobe analysis was performed using standard quantitative analysis procedures to determine precision and sensitivity.

The microstructure of the four Ti-8Al-1V-1Mo heats are classified as alpha or near alpha alloys. The microstructure of the 811 specimens consists of alpha grains in a matrix of beta and alpha. Composition of the grain interior and grain boundaries of each were analyzed independently by the EPM.

A compositional variation was found between grain interiors and grain boundaries after EPM analysis. A higher than nominal aluminum content was measured in the grain interiors (alpha) and a lower aluminum content in the grain boundaries (beta). The compositional variation of vanadium and molybdenum occurred in the opposite direction to that of aluminum. Additionally, the variation in composition of aluminum between phases in the 811 alloys was found to be smaller in magnitude for the mill anneal/furnace cool heats as compared to the mill anneal/air cool specimens.

The microstructure of the Ti-6Al-4V alloys is equiaxed alpha grains in a transformed beta matrix and for the Ti-13Cr-11V-3Al alloy is in the duplex anneal condition exhibiting particles of precipitated alpha in beta grains. In both alloys, the alpha phase had an increased aluminum content, while the beta grains showed a lower than nominal aluminum content with respectively higher vanadium and chromium contents.

The level and extent of alloy element segregation with respect to the microstructure of these commercial alloys has been experimentally determined. These results will now be used to assess the role of microsegregation on the mechanical and corrosion properties of these alloys.

CRYSTAL GROWTH BY VAPOR TRANSPORT REACTIONS

Senior Investigator: H. Wiedemeier

Crystal growth by vapor transport is a widely used technique for the preparation of single crystals of research quality and for the industrial fabrication of single crystalline materials. This technique has proven to be particularly useful for the production of mixed or alloy type single crystals and of epitaxial layers which are of great practical importance for solid state devices. The experimental details of the vapor transport technique have been discussed in several publications resulting from our laboratory and by other workers in the field.

In view of the increased importance of alloy type semiconductors, our studies of the germanium selenide and telluride systems have been extended to the investigation of the formation of mixed single crystals. A prerequisite of such studies is the knowledge of the room and high temperature phase diagram of the system. The temperature-composition phase diagram of the GeSe-GeTe system is presently under investigation.

Mixtures of various molar GeSe-GeTe ratios over the entire composition range are fused in evacuated closed silica ampules at temperatures of about 750°C for several hours. The reaction product is cooled to room temperature according to a programmed cooling cycle. The degree of solid solution and the type and number of phases present are determined by X-ray diffraction techniques. GeSe has a distorted NaCl-type orthorhombic structure and GeTe has a normal NaCl-type structure above approximately 400°C and a rhombohedrally distorted NaCl structure below 400°C.

Present results based on room temperature X-ray diffraction data indicate that GeSe is soluble in GeTe to about 50 mole % and that the solid solutions have the rhombohedral structure. The degree of solid solution of GeTe in GeSe extends to about 10 mole % GeTe and the resulting one-phase region has the orthorhombic structure. In addition, a third one-phase region extending from about 65 to 85 mole % GeSe is observed in this system. Alloys within the latter one-phase region have a hexagonal structure which is not common to any of the end components. The three one-phase regions are separated by two-phase regions and the lattice parameters of compositions within the one-phase regions change linearly as a function of composition. This observation supports the conclusion that the hexagonal phase is not a new compound with a wide homogeneity range, but rather a solid solution with a new structure (with respect to the end components).

Vapor transport studies on compositions within the one-phase regions indicate that the single crystalline transport product is affected by the composition and structure of the source material. Based on present results, alloy compositions with rhombohedral or orthorhombic structure yield crystals of varying compositions while the hexagonal alloys yield single crystal platelets of the same structure and closer in composition to the source material. Work is in progress to define transport conditions for the reproducible growth of alloy single crystals of these systems.

The studies on the room temperature phase diagram of the GeSe-GeTe system are being continued and will be extended to higher temperatures. These efforts will help to clarify existing discrepancies in a technologically important system.

22-A

PHYSICAL PROPERTIES AND STRUCTURE OF AEROSPACE MATERIALS

PHYSICAL PROPERTIES AND STRUCTURE OF AEROSPACE MATERIALS

Seven projects are currently active in this area. "An Atomistic Approach to the Strength of Interfaces" concerns experimental observation of the interaction of metal vapors with oxide surfaces and is presently reporting on development of techniques for producing clean oxide surfaces.

Three projects, "Low Temperature Thermal Properties of Amorphous Solids," "Relaxation in Amorphous and Crystalline Materials at Low Temperatures," and "NMR in Polymers," are at this time reporting complementary data on the effects of molecular oxygen on low temperature properties of polymers. Absorbed oxygen appears to play an unanticipated but significant role in low temperature responses of these materials.

"Thermal Conductivity of Composites" is concerned with enhancement of heat transfer characteristics of poor conductors by filling with conductor particles. This report is on carbon fiber-filled epoxy materials.

From the project, "Dilatometric and X-Ray Thermal Expansion Measurements in Tetragonal Tin," we have a report on completion of high accuracy measurements of thermal expansion in the 30 to 150°C range and a conclusion that the predominant crystallographic defect in this material is lattice vacancies.

The project, "Radiative Transfer Studies for Spacecraft Coatings," reports on the beginning of experiments to characterize the optical properties of three model coatings systems based on TiO_2, ZnO and $BaSO_4$.

AN ATOMISTIC APPROACH TO THE STRENGTH OF INTERFACES

Senior Investigator: J. B. Hudson

This project involves the study of the energetics and kinetics of the interaction of metal vapors with clean and contaminated oxide surfaces, by a combination of mass spectrometric molecular beam and Auger electron spectrometric techniques. The aim of the work is to determine the relationship between interatomic binding forces and bulk interfacial strength.

During the present reporting period efforts have been concentrated on means of producing a clean, well characterized oxide surface. Efforts to produce such surfaces by repeated cleavage of a crystal in ultrahigh vacuum have been abandoned, at least for the present, as it has not proven feasible to perform the many repeated cleavages needed for efficient use of the molecular beam technique. We are now attempting to produce the desired surfaces by a combination of argon ion bombardment followed by annealing in a partial pressure of oxygen. The Auger electron spectrometry system developed in a previous period is now operational, and is being used to monitor surface cleanliness.

We have also developed a variable frequency molecular beam modulation system, which permits chopping of the incident beam of metal atoms at frequencies up to 500 cycles per second. This will permit measurement of stay times in the adsorbed state down to roughly 10^{-4} seconds, about a factor of 100 shorter than attainable with previous techniques, and thus greatly facilitate studies of relatively weak interactions.

LOW TEMPERATURE THERMAL PROPERTIES OF AMORPHOUS SOLIDS

Senior Investigator: G. L. Salinger

The low temperature specific heat capacity of all amorphous materials can be described by $c = aT + bT^3$ where b is larger than that calculated from Debye theory and the linear term can not be due to electrons since these materials are excellent insulators. The origin of these anomalies is being investigated to determine their structural origin.

Pulsed nuclear magnetic resonance experiments, done jointly by P. A. Casabella and us, show that molecular oxygen dominates the relaxation below 30 K. We have shown that the specific heat of polystyrene below 1 K is not affected by molecular oxygen. It may be, however, that molecular oxygen is responsible for some of the anomalies in the specific heat above 1 K. This will be investigated in the near future.

Cross linking polystyrene does not change the linear term but does reduce the value of b considerably, indicating that local vibrations of pendant groups may be responsible for the excess cubic term but not the linear term.

The specific heat capacity of polyethylene as previously measured has been plotted versus crystallinity as determined by nuclear magnetic resonance techniques [done by P. A. Casabella and Mrs. Borton]. The results indicate that the linear term is contributed entirely by the amorphous material.

The above studies are being reoriented to elucidate the properties of materials useful as insulators in the cryogenic transmission of power.

Electrical resistivity has been measured as a function of temperature in a sample of glassy carbon to determine the electronic contribution to the thermal conductivity. Other samples of differing heat treatments will also be measured. This will aid in the interpretation of measurements reported earlier.

These studies were also partially funded by the National Science Foundation and a DoD Themis Grant.

RELAXATION IN AMORPHOUS AND CRYSTALLINE MATERIALS AT LOW TEMPERATURES

Senior Investigators: R. K. MacCrone
G. L. Salinger

The relative modulus and mechanical loss in a number of polymers and glasses is being measured as a function of temperature to study the localized modes which give rise to the low temperature specific heat anomalies found in these amorphous materials. The structural origin of these modes is the subject of current intense investigation, and we believe that a comparative study of those materials which show this anomaly will enable the structural origin to be determined. Conversely, once the structural origin of these modes is understood, this technique can be used to determine the structure of other materials, for instance, the polyimides which are of interest to NASA. Furthermore, these materials are useful as insulators in the cryogenic transmission of power. To be useful in this application, the material should have no loss peaks at low temperature.

Pulsed nuclear magnetic resonance experiments, done by P. A. Casabella and R. A. Oliva, together with G. L. Salinger, have shown that molecular oxygen dominates the relaxation below 30K. Internal friction has been measured on samples of polycarbonate (Lexan) and a specially molded sample of polymethyl methacrylate. Samples having the oxygen removed (by pumping for three days at $60^{\circ}C$) show a much reduced modulus change with increasing temperature than those not deoxygenated. However, the loss peaks observed appear not to have changed.

Work continues on the SiO_2 samples. The samples doped with Al_2O_3 and Na_2O have been returned to Corning to be recast.

NMR IN POLYMERS

Senior Investigator: P. A. Casabella

The study of the proton spin-lattice relaxation time in polymers at low temperatures has continued. In the previous progress report on this topic it was reported that the data from polymethyl methacrylate could be interpreted in terms of a rotational tunneling of one of the methyl groups. The particular feature that led to the conclusion was a minimum in a plot of spin-lattice relaxation time vs. temperature at 10 K.

However, further study showed that similar minima exist in plots of relaxation time vs. temperature for polyethylene and polystyrene, neither of which contain methyl groups. It is now believed that the low temperature behavior of the spin-lattice relaxation time is determined mainly by paramagnetic oxygen molecules that have diffused into the material.

To test this hypothesis, all three samples were de-gassed by heating to temperatures of 60°C to 100°C in a vacuum oven for about one week. After this treatment the low temperature minimum in the relaxation time graph disappeared in all three cases, and the relaxation time increased by about two orders of magnitude. Before de-gassing the relaxation times at 4.2 K are close to one second. After a few weeks' exposure to the air at room temperature, the samples again exhibit the shorter relaxation times and the minimum at 10 K.

The presence of enough oxygen to produce such effects could affect other measurements as well. These results have been passed on to G. L. Salinger and R. K. MacCrone who will repeat their experiments on de-gassed samples to determine whether the effects they have noted are affected by oxygen or any other atmospheric gas.

In addition, a study of the crystallinity of polyethylene by NMR techniques has been completed. Broad line proton NMR spectra of several samples of polyethylene, taken at room temperature, were interpreted as being due to three different phases of the material. Each resonance was assumed to be a superposition of a resonance from crystalline material, a resonance from amorphous material, and a resonance from the boundary region between the other two phases. The experimental resonances were broken down into their components by computer, and the amplitudes of the components provided a measure of the proportion of each phase present. The proportion of the amorphous phase was of considerable interest to G. L. Salinger who was able to correlate these results with his low temperature specific heat data as described elsewhere in this report.

THERMAL CONDUCTIVITY OF COMPOSITES

Senior Investigator: D. Hansen

Previously, we have reported data on the enhancement of thermal conductivity in a resin by loading with 5 to 8% of copper particles of length to diameter ratio from 20 to 100. Conductivity was increased as much as 34 fold with an essentially random dispersion of filler particles.

In experiments conducted during this period, we have obtained similar results in composites of carbon fiber in epoxy resin. Before reporting the carbon fiber data in full, we need to complete specimen characterizations of fiber particle orientation and some measurements of electrical resistivity of the composites.

During the next report period, we expect to complete our experiments on the carbon fiber composites and will begin some on boron nitride fiber-filled systems. Boron nitride, presumably, should be equally as effective as carbon fiber in enhancing thermal conductivity while not significantly influencing the electrical resistivity.

DILATOMETRIC AND X-RAY THERMAL EXPANSION MEASUREMENTS IN TETRAGONAL TIN

Senior Investigator: H. B. Huntington

Studies of axial thermal expansion in non-cubic crystals can give very reliable information on the density of vacancies and, in addition, yield insight into the mechanism of point defect creation and annihilation in well annealed single crystals and into the dislocation densities and climb rates along the respective symmetry directions. Since the net defect concentration is small even at the melting temperature (usually in the range of 5×10^{-4}), considerable care is necessary to obtain accuracy of the order of 10 parts per million in the fractional length increase, $\Delta\ell/\ell_0$, and temperature uniformity over the length of the sample of 0.1°C at each equilibrium temperature.

Such high accuracy measurements on the thermal expansion along the two principal axial directions of tetragonal tin have been completed using two critically oriented single crystal tin bars of length 15 cm. and 1 x 1 cm. square cross section. The points form a smoothly varying curve of $\Delta\ell/\ell_0$ vs. T with a maximum deviation of less than 10 parts per million over the entire measured range. The expansion was reproduced over repeated heating and cooling cycles for each crystal. Least square fits in 10°C intervals using 4 to 7 data points each yielded thermal expansion coefficients in close agreement with the earlier measurements.

The closeness of the thermal expansion coefficients at low temperature to a strictly linear increase with temperature for both axial and volume coefficients tempts one to fit the lattice contribution to the thermal dilation with a parabolic function. Preliminary work, fitting the $\Delta\ell/\ell_0$ data to a parabola in the range 30° - 150°C and comparing the calculated lattice expansion to the high temperature data, has been completed. The results indicate that the predominant defect is lattice vacancies with an energy of formation of 0.46 ev (which is consistent with available resistivity and specific heat measurement).

We have in mind possible measurements of the high temperature lattice parameters with the available X-ray diffractometer as a further check of the results.

RADIATIVE TRANSFER STUDIES FOR SPACECRAFT COATINGS

Senior Investigator: F. W. Billmeyer, Jr.

Effort over the past period has been concentrated on the preparation of samples for a model system simulating actual spacecraft coatings.

Further studies of the polyvinyl chloride latices described in the last report have led us to abandon them as models for the zinc orthotitanate (Zn_2TiO_4) pigment actually used for two reasons: (1) The latices have a far lower scattering efficiency than Zn_2TiO_4 due to their much lower refractive index. While we do not deem it necessary to match refractive indices exactly, a very large difference might lead to an entirely different sort of optical behavior. (2) The latices are nearly monodisperse, unlike real pigments, and may pack in ordered arrays giving rise to undesired diffraction effects.

We expect to use three different pigments in various model systems: TiO_2 (refractive index $n \simeq 2.7$), ZnO ($n \simeq 2.0$), and $BaSO_4$ ($n \simeq 1.64$). The binder, as explained below, will probably be a long-chain aliphatic alcohol with $n \simeq 1.4$. At least one of the above pigments (TiO_2) can be obtained in a variety of particle sizes and particle-size distributions. These choices allow us to test the effects of relative refractive index and particle size and distribution individually on the optical behavior of the samples. We also hope that our sample size requirements will be such that eventually we can utilize Zn_2TiO_4 despite the very small quantities available.

Our current method of sample preparation consists of mixing pigment and matrix liquid in the desired proportions. These are selected so that there is not enough liquid to fill all the voids between pigment particles, leading to a pigment-matrix-void system modeling a paint film above the critical pigment volume concentration (CPVC).

Since the binder is a liquid of as low viscosity as can be obtained commensurate with requirements of low volatility and wetting the pigment, it distributes uniformly in a very short time. This rapid equilibration is well known and is characteristic, for example, of the penetration of water into soils.

The paste-like mixture is pressed into thin glass cells of known thickness (a fraction of a millimeter) for the optical measurement. It may be possible to reduce the amount of matrix liquid on demand by controlled evaporation and subsequent redistribution, so that a single sample can serve for measurements at a variety of concentrations above the CPVC.

During the coming period we expect to finalize our sample preparation techniques and complete the development of reliable optical measurement methods. We will also start consideration of the appropriate turbid-medium theory to yield scattering cross sections from the optical data obtained.

34-A

REPRINTS SUBMITTED TO NASA

THESES COMPLETED

MEMBERS OF FACULTY COMMITTEE ON INTERDISCIPLINARY MATERIALS RESEARCH

PERSONNEL LIST

AUTHOR INDEX

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Author	Title	Degree
Aitken, J.	Bound Polaron Behavior in the Low Temperature Regime	Ph.D.
Bhat, T. A.	The Strength Differential Effect in Maraging Steels	Ph.D.
Borton, H.	Determination of Polyethylene Crystallinities by NMR	M.S.
Dening, D. C.	The Relation of Nuclear Quadrupole Coupling to Spontaneous Polarization	Ph.D.
Halsey, J. L.	The Function of Rubbery Domains in a Glassy Matrix After Craze Initiation as Determined by Scanning Electron Microscopy	M.S.
Ho, T. C.	Biaxial Stress Relaxation Studies of Polymethylmethacrylate in the Glassy State	Ph.D.
Myers, F. A.	Biaxial Stress Yielding of Polymethylmethacrylate	M.S.
Oliva, R. A.	Spin-Lattice Relaxation Times in Polymers at Low Temperature	Ph.D.

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AUTHOR INDEX